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Carbon

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Robust nanoporous alumina monoliths by atomic layer deposition on low-density carbon-nanotube scaffolds

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Abstract

Synthesis of nanoporous alumina monoliths with controlled morphology and density is a challenge. Here, we demonstrate mechanically robust alumina monoliths synthesized by conformal overcoating of graphitic nanoligaments of low-density carbon-nanotube-based aerogels (CNT-CAs) by using atomic layer deposition. Young's modulus of resultant monoliths increases superlinearly with the monolith density with an exponent of ~ 2.4, defined by the morphology and connectivity of the CNT-CA scaffold. As a result, for a given monolith density, alumina-carbon composites have moduli comparable to those of CNT-CAs and significantly superior to those of pure alumina aerogels reported previously.

1. Introduction

Aerogels are low-density, open-cell nanoporous materials with typical porosities of $\gtrsim 80\%$. They are made of randomly interconnected high-aspect-ratio nanoligaments of complex geometry that could often be approximated

as curved rods, strings of interconnected spherical particles, or thin sheets. With high surface areas, tunable monolith densities, and control over the elemental composition and geometry of ligaments, potential applications of aerogels are numerous.[1] In particular, alumina aerogels,[2–9] which are the focus of the present work, are attractive as high-temperature catalysts or catalytic supports, structural ceramics, high-temperature thermal insulators, and adsorptive separators.

However, synthetic routes to monolithic alumina aerogels are currently limited. Two main sol-gel-based approaches to the synthesis of alumina aerogels have been reported. In the first approach, alumina aerogels have been prepared with alkoxide precursors.[3–6] Due to high reactivity of the alkoxide precursors, synthesis of uniform macroscopic monoliths with this method is difficult. The second approach overcomes this limitation by using aluminum salts ($AlCl_3 \cdot 6H_2O$ or $Al(NO_3)_3 \cdot 9H_2O$) instead of the reactive alkoxide precursors. [7] In such salt-derived alumina aerogels, the crystallographic phase and geometry of nanoligaments are controlled by the choice of the precursor salt [7] and by post-synthesis thermal annealing, which causes material dehydration (i.e., conversion of $AlOOH$ into Al_2O_3) and curling of nanoleaflet-like ligaments. [8] Although such alumina aerogels with nanoleaflet-like ligaments have greatly improved mechanical properties compared to the other alumina aerogels reported, [8] their stiffness remains inferior to that of more mechanically robust carbon aerogels. In particular, carbon-nanotube-based carbon aerogels (CNT-CAs), recently developed by Worsley and coworkers, [10] are approximately ~ 3 times stiffer than the "robust" salt-derived alumina aerogels with nanoleaflet-shaped ligaments. [10, 11]

Here, we report a templating method of the synthesis of alumina aerogels by conformally overcoating nanoligaments in low-density CNT-CA scaffolds with alumina using atomic layer deposition (ALD). The resultant nanoporous alumina-carbon composites have mechanical properties significantly superior to those of pure alumina aerogels, with the scaling law of Young's modulus on the monolith density determined by the morphology and connectivity of the starting low-density CNT-CA scaffold.

2. Experimental

Three sets of monolithic CNT-CAs with a CNT loading of 25-50 wt.% and densities of 30, 60, and 125 mg cm^{-3} were prepared as described in detail elsewhere. [10] In brief, purified single-walled CNTs (Carbon Solutions, Inc.) were dispersed in water in a sonication bath. The sol-gel precursors (resorcinol and formaldehyde) and the polymerization catalyst (NaCO$_3$) were added, and the mixture gelled. Wet gels were washed with acetone, dried with supercritical CO$_2$, and pyrolyzed at 1050 °C under N$_2$.

Nanoligaments of as-synthesized CNT-CAs were conformally coated with alumina layers by alternating exposures to trimethyl-aluminum (TMA, which is Al(CH$_3$)$_3$) and water precursors in a warm wall ALD reactor (Kurt J. Lesker), as described elsewhere. [12, 13] During the deposition, reactor walls and the sample stage were kept at 100 and 125 °C, respectively. The aerogel samples were repeatedly exposed to the following sequence: TMA pulse, Ar purge, H$_2$O pulse, and Ar purge. The pressure during TMA and H$_2$O pulses was 0.8 Torr and 1.2 Torr, respectively. Long pump, pulse, and purge cycles (20, 500, and 500 s, respectively) were used for uniform coatings throughout

nanoporous monoliths. [14]

Monolith densities of resultant carbon-alumina composites were determined based on the initial densities of CNT-CAs and the elemental composition measured by Rutherford backscattering spectrometry (RBS) with a 2 MeV ^{4}He ion beam. Selected samples were examined by scanning electron microscopy (SEM) in a JEOL 7401-F microscope operated at 2 kV and by bright-field transmission electron microscopy (TEM) in a FEI TF-20 Tecnai microscope operated at 200 kV. For TEM imaging, CNT-CAs were dispersed on holey carbon grids with an ultrathin (< 3 nm) carbon support film. Selected samples were also analyzed by ultra-small angle x-ray scattering (US-AXS) with a double-crystal Bonse-Hart instrument at beamline 15ID-D at the Advanced Photon Source, Argonne National Laboratory. The x-ray energy was 16.9 kV. Slit-smeared USAXS data were corrected for background scattering, calibrated against a reference sample, and desmeared with Irena software tool suite. [15] Irena suite [15] was also used to fit desmeared scattering profiles with a model assuming scatterer size distributions with carbon cylinder and carbon-core/alumina-shell cylinder form factors for uncoated and alumina-coated CNT-CAs, respectively.

Mechanical properties were studied by indentation in the load-controlled mode in an MTS XP nanoindenter with a flat punch diamond tip with an effective diameter of 62 μm, which is much larger than the size of individual ligaments or pores ($< 0.1\ \mu$m). Before indentation, monoliths were machined with a cylindrical endmill, yielding macroscopically flat surfaces. Both loading and unloading rates were kept constant to maintain an indentation strain rate of 10^{-3} s^{-1}. [16] Stiffness was characterized by indentation Young's mod-

Figure 1: (a)-(c) SEM and (d)-(f) bright-field TEM images of representative aerogels. (a),(d) Uncoated CNT-CAs. CNT-CAs (b),(e) after 20 cycles and (c),(f) after 100 cycles of alumina ALD. Scale bars for SEM and TEM images are 1μm and 50 nm, respectively.

ulus, which was calculated based on the initial slope of the unloading curve according to the Oliver-Pharr method. [17] In Oliver-Pharr calculations, we assumed Poisson's ratios of diamond and aerogels of 0.07 and 0.2, respectively, and a Young's modulus of diamond of 1141 GPa. [16, 18]

3. Results and discussion

Figure 1 shows representative SEM and TEM images of uncoated and alumina-coated CNT-CAs. Consistent with previous reports, [10] CNT-CAs form a network of ligaments made from CNT bundles decorated and interconnected by carbon layers and nanoparticles. After ALD, ligaments are conformally coated with alumina, resulting in an increase in their average thickness [see TEM images in Figs. 1(d)–1(f)], with the foam morphology and ligament connectivity determined by those of the starting CNT-CAs [see SEM images in Figs. 1(a) – 1(c)]. The graphene surface of defect-free CNTs is chemically inert and is expected to exhibit poor nucleation with the deposition of isolated alumina particles instead of conformal layers during alumina ALD. [19] Hence, the conformal coating revealed by TEM images of Figs. 1(d)-1(f) suggests that the disordered graphitic carbon coating on CNT bundles of CNT-CA nanoligaments provides nucleation sites for the adsorption of TMA.

Figure 2: USAXS profiles of CNT-CA samples exposed to alumina ALD with different number of cycles, as indicated in the legend. Symbols are experimental data, and solid lines are fits with a model described in the text. Monolith densities are 30, 75, and 240 mg cm^{-3} for the samples exposed to 0, 20, and 100 ALD cycles, respectively.

Quantitative information about the morphology of CNT-CAs, complementing electron microscopy observations, has been obtained by USAXS, which is one of the most common tools for studying aerogel morphology. [1] Figure 2 shows representative USAXS profiles for an uncoated CNT-CA and CNT-CAs coated with 20 and 100 ALD cycles of alumina. All three profiles of Fig. 2 are rich in features, reflecting the complex morphology of these aerogels. The profile from the uncoated CNT-CA is the simplest. It exhibits a Guinier knee at a scattering vector q of $\sim 2 \times 10^{-2}$ Å^{-1} and a Porod power-law region with a slope of ~ -4 at $q > 5 \times 10^{-2}$ Å^{-1}, reflecting scattering from CNT-CA nanoligaments.

After ALD deposition, Fig. 2 reveals that the overall scattering intensity increases, which could be attributed to larger scattering contrast of alumina. [2] The Guinier knee shifts to lower q, consistent with an increase in the nanoligament width. Several new scattering features associated with the alumina coating appear in the range of $q > 10^{-2}$ Å^{-1} and become more evident with increasing number of ALD cycles. Their oscillatory behavior precludes the use of the standard Guinier or Porod analysis and suggests a uniform dis-

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[2]Calculated x-ray scattering contrast of graphite and Al$_2$O$_3$ is 314 and 1080 $\times 10^{20}$ cm^{-4}, respectively. [15]

tribution of scatterers with a narrow size distribution. [20] Hence, given the cylinder-like shape of nanoligaments revealed by TEM [Figs. 1(d) – 1(f)], we have used a scattering population comprising of carbon cylinders and carbon-core/alumina-shell cylinders to represent uncoated and alumina-coated CNT-CAs, respectively, in the q region of $q > 10^{-3}$ Å^{-1}. The log-normal size distribution of these scatterers has been obtained by fitting experimental USAXS profiles to the scattering model with a least-square algorithm with Irena software suite. [15] An additional unified level model with a Porod slope of ~ -2.7 was used to fit the scattering curve in the low q region ($q < 10^{-3}$ Å^{-1}) for both uncoated and alumina-coated samples, accounting for scattering from larger scale agglomerates of nanoligaments.

The structural parameters derived from such a fitting of USAXS data are given in Table 1. Note that the fits are not sensitive to the cylinder length above ~ 200 nm. As expected, the alumina layer thickness and the volume fraction occupied by the solid in the monolith increase with the number of ALD cycles. The densities estimated based on the volume fraction occupied by samples exposed to 0, 20, and 100 ALD cycles are 19, 82, and 240 mg cm^{-3}, respectively. These are in reasonable agreement with the densities determined by RBS measurements (30, 75, and 240 mg cm^{-3}). Importantly, the agreement between USAXS and TEM results suggests that electron microscopy observations of Fig. 1 are representative of the ligament morphology in macroscopic samples despite the inherently microscopic volumes studied in the TEM.

The preservation of ligament connectivity of CNT-CAs after ALD coating is further supported by mechanical deformation data of Fig. 3, showing

Table 1: Parameters of USAXS profile fitting with a model described in the text.

Parameter	Pristine	20 ALD cycles	100 ALD cycles
Carbon cylinder diameter (Å)	130	130	130
Alumina shell thickness (Å)	0	40	199
Vol. fraction (%)	0.85	2.70	7.36

the dependence of Young's modulus (E) on the monolith density (ρ) for uncoated and alumina-coated CNT-CAs. The density scaling law of E of low density solids can often be expressed as $\frac{E}{E_s} \propto (\frac{\rho}{\rho_s})^n$, where E_s and ρ_s are Young's modulus and the density of the ligament material, respectively. [21] For a perfectly interconnected open cell structure with bending as the dominant deformation mechanism, $n = 2.0$. The exponent n, however, depends on the shape, curvature, uniformity, and connectivity of ligaments and is difficult to predict, given the complex morphology of most aerogels. [8, 10, 11, 22, 23] The value of n is expected to increase with an increase in the degree of imperfection of ligament connectivity. Hence, n could be used for semi-quantitative description of ligament connectivity. Plotted as a solid line in Fig. 3 is the experimental $E(\rho) \propto \rho^{2.4}$ dependence for uncoated CNT-CAs, taken from Ref.11. Interestingly, Fig. 3 reveals that the $E(\rho)$ dependence for all three sets of CNT-CA coated with alumina closely follows the $E(\rho)$ curve of uncoated CNT-CAs, supporting the above finding of the preservation of ligament connectivity upon ALD overcoating. Furthermore, Fig. 3 shows that, after 100 ALD cycles, alumina-carbon composites have stiffness values even larger than those of CNT-CAs of equivalent densities. This could be attributed to additional interconnects between ligaments for

Figure 3: Young's modulus of uncoated and alumina-coated CNT-CAs as a function of the monolith density. Different symbols represent data for samples derived from three different starting densities of uncoated CNT-CAs of 30, 60, and 125 mg cm^{-3}, as indicated in the legend. The solid line is a power-law fit to data for uncoated CNT-CAs taken from Ref.11.

a regime when the resultant ligament thickness is comparable to the average distance between ligaments (i.e., the effective pore size) in the starting CNT-CA.

Notably, throughout the entire density range studied, ALD-derived alumina aerogels are $\sim 2-10$ times stiffer than pure alumina aerogels reported previously. [6, 8] This demonstrates the potential of the ALD templating approach to synthesize novel nanoporous solids. For example, we have also extended the present approach to ALD-derived carbon-alumina composites by coating conventional carbonized resorcinol-formaldehyde (cRF) aerogels. [24] We have found that, similar to results of Fig. 3, the dependence of Young's modulus on the monolith density of alumina coated cRF gels follows the scaling law of the starting cRF scaffold.

4. Conclusions

In summary, we have demonstrated robust nanoporous alumina monoliths synthesized by ALD on low-density carbon nanotube aerogels. Alumina conformally coats aerogel ligaments. The dependence of Young's modulus on the density of resultant monoliths closely follows the scaling law defined by the initial carbon aerogel scaffold. The nanoporous alumina monoliths syn-

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thesized with this method exhibit superior stiffness (for equivalent monolith densities) than the pure nanoporous aluminas reported previously.

Acknowledgements

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